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SOME PROBLEMS IN THE RHEOLOGICAL
CHARACTERISATION OF COMPOSITE ROCKET
PROPELLANTS

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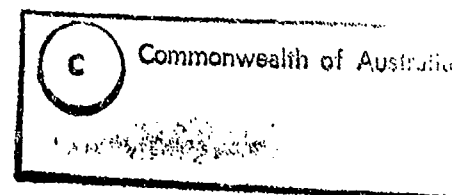
R.C. WARREN

MRL-TN-642

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Some Problems in the Rheological Characterisation of Composite Rocket Propellants

R.C. Warren

MRL Technical Note
MRL-TN-642

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Abstract

Apparent viscosities of a composite propellant analogue were measured with both rotary and extrusion instruments. A Haake Viscometer in the Couette configuration was used with 2 gap widths and also with a profiled cup and rotor. An extrusion rheometer was fitted with a slit die and measurements were made at 2 slit thicknesses. The flow was found to be time dependent, and there was apparent slip at the wall. It is suggested that the cause of this behaviour is filler particle migration in the non-uniform stress fields. The filler migration is assumed to cause a layer of binder to develop at the walls confining the flow, and this layer would lubricate the flow of the bulk of the material causing an apparent slip. The effect of the slip is to reduce the apparent viscosity of the material, which also appears to be affected by ageing of the samples under ambient conditions for several days. Particle sizes of the solid ingredients were also measured.

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Some Problems in the Rheological Characterisation of Composite Rocket Propellants

1. Introduction

A meeting of a panel of experts in the field of rheology of energetic materials in 1987 concluded that the entire energetic materials industry had grossly underestimated the importance of rheology and its impact on the production, performance and vulnerability characteristics of materials. The introduction of continuous production technology for energetic materials, which was occurring in many countries, was seen to require a sound understanding of the rheological properties which control the process. As a result of the findings of the panel the TTCP Technical Panel W-4 set up Key Technical Area 12 (KTA-12) on Rheology of Energetic Materials to establish a common basis for the measurement of rheological properties of energetic materials. The aim was in part to identify the important parameters which must be evaluated to adequately characterise rheological properties, identify existing and emerging diagnostic technologies to measure these parameters, and provide a common database to guide further developments in this field.

The main activity of the KTA was the distribution of standard materials to each participating agency for characterisation by whatever methods deemed appropriate. Since the main area of concern was the behaviour of highly filled composite materials such as uncured composite rocket propellants and polymer bonded explosives, an inert system simulating these materials was chosen for study. The materials distributed were: HTPB binder, ammonium sulphate in coarse (200 micron) and fine (20 micron) forms to simulate ammonium perchlorate commonly used in propellants, aluminium powder, isophorone diisocyanate (IPDI), and an uncured master batch mixed from the ingredients. The composition of the master batch was chosen to have the same composition by volume as an uncured rocket propellant containing 14% HTPB, 15% aluminium and 71% ammonium perchlorate by weight. The curative was not included as the properties of the material before cure were of interest, and other possible ingredients were omitted to avoid any extraneous factors affecting the results.

Unfortunately, when the master batch was received by most participants, including Australia, it had sedimented and partially polymerised. In order to carry out the rheological part of the KTA program, a new batch had to be prepared. This paper reports some rheological measurements on the batch of propellant simulant produced from the ingredients provided, and particle size measurements of the solid ingredients.

2. Particle Size

2.1 Equipment

Two series of particle size measurements were made on the solid ingredients. The first was done in September 1990 on a Malvern LBD 2200 analyser. The aluminium and fine ammonium sulphate were analysed using a 300 mm focal length lens, and the coarse ammonium sulphate was analysed using a 1000 mm lens. All samples were dispersed in Sedisperse A11, using Twitchells Base to aid dispersion. Samples were stirred in the dispersing medium for two minutes before testing. At least two runs per sample were done.

The second series of measurements was done one year later on both the Malvern LBD 2200, and a new Malvern Mastersizer/E. On the new analyser the aluminium was analysed with a 100 mm focal length lens and the ammonium sulphate was analysed with a 300 mm focal length lens. The sample preparation was the same as in the first series.

2.2 Results and Discussion

Typical results from the Malvern Mastersizer/E are given in Figures 1 to 3, and the results of all the particle size measurements are summarised below. Also shown are the values obtained at the Naval Ordnance Station, Indian Head which were provided with the material. The values quoted are medians of the size distributions, but the Indian Head data was also given as the means of the distributions.

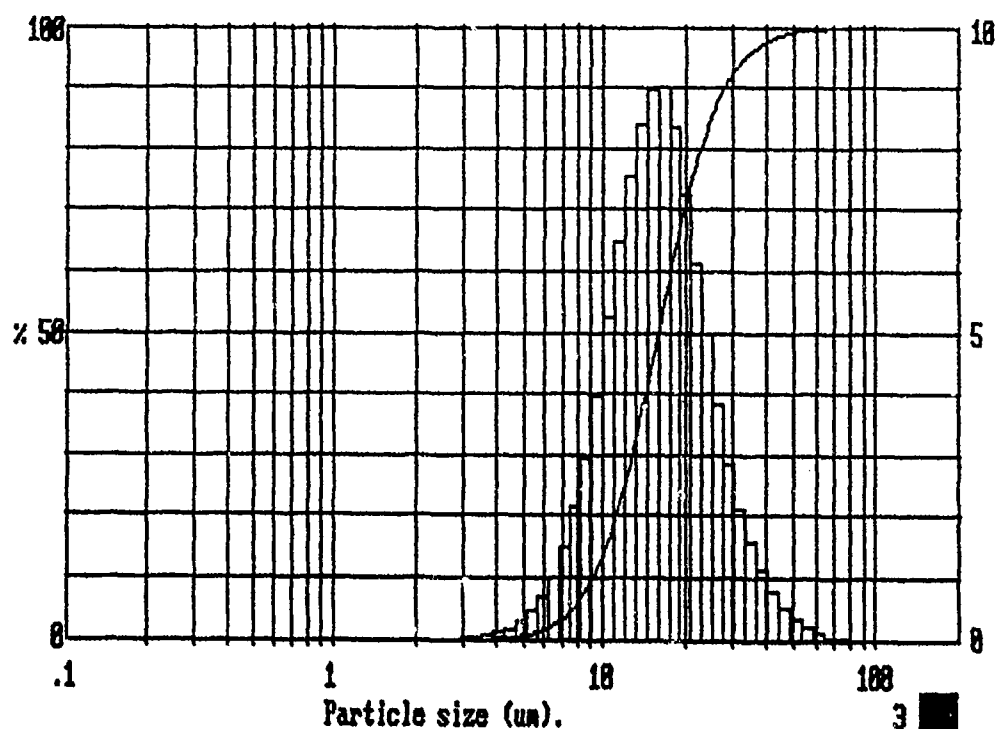
Material	Median Size (μm)			
	LBD 2200		Mastersizer/E	NOS.IH
	1st run	2nd run		
Aluminium	16.5, 17	16, 16	15.8, 16.7	17.3
Ammonium Sulphate (C)	140, 185	165, 175, 130, 140	192, 195	-
Ammonium Sulphate (F)	38, 41	69, 70	56.4, 52.6	66.6

MALVERN MasterSizer/E SB.0B Easy Mode 08 Aug 1919 3:55 pm

High Size	Under %	High Size	Under %	High Size	Under %	High Size	Under %	High Size	Under %	High Size	Under %	Span
												1.17
180	100	64.4	99.9	23.0	81.3	8.25	6.7	2.95	0.1	1.06	0.0	D[4,3]
164	100	58.7	99.8	21.0	75.1	7.51	4.6	2.69	0.0	0.96	0.0	17.49µm
149	100	53.4	99.5	19.1	67.9	6.84	3.0	2.45	0.0	0.88	0.0	
136	100	48.7	99.2	17.4	59.5	6.23	2.0	2.23	0.0	0.80	0.0	D[3,2]
124	100	44.3	98.7	15.9	50.5	5.67	1.3	2.03	0.0	0.73	0.0	14.30µm
113	100	40.4	97.9	14.4	41.5	5.17	0.9	1.85	0.0	0.66	0.0	
103	100	36.8	96.8	13.2	33.0	4.71	0.5	1.68	0.0	0.60	0.0	D[v,0.9]
93.6	100	33.5	95.2	12.0	25.4	4.29	0.3	1.53	0.0	0.55	0.0	27.67µm
85.2	100	30.5	93.0	10.9	18.9	3.91	0.2	1.40	0.0	0.50	0.0	
77.6	100	27.8	90.1	9.94	13.6	3.56	0.1	1.27	0.0			D[v,0.1]
70.7	99.9	25.3	86.3	9.05	9.7	3.24	0.1	1.16	0.0			9.13µm
Source = Data:p81-91c												D[v,0.5] 15.79µm
Record No. = 1												
Focal length = 100 mm												
Presentation = std												
Beam length = 15.0 mm				Residual = 0.618 %				Model indp				
Obscuration = 0.1968				Volume Conc. = 0.0067%				Sp.S.A 0.4195 m²/cc.				
Volume distribution												

7033 std IM10133Y
Aluminum Powder
LR P81/91 8th August 1991

MALVERN MasterSizer/E SB.0B Master Mode 08 Aug 1919 3:55 pm



7033 std IM10133Y
Aluminum Powder
LR P81/91 8th August 1991

Figure 1: Typical aluminium particle size data from Malvern Mastersizer/E analyser.

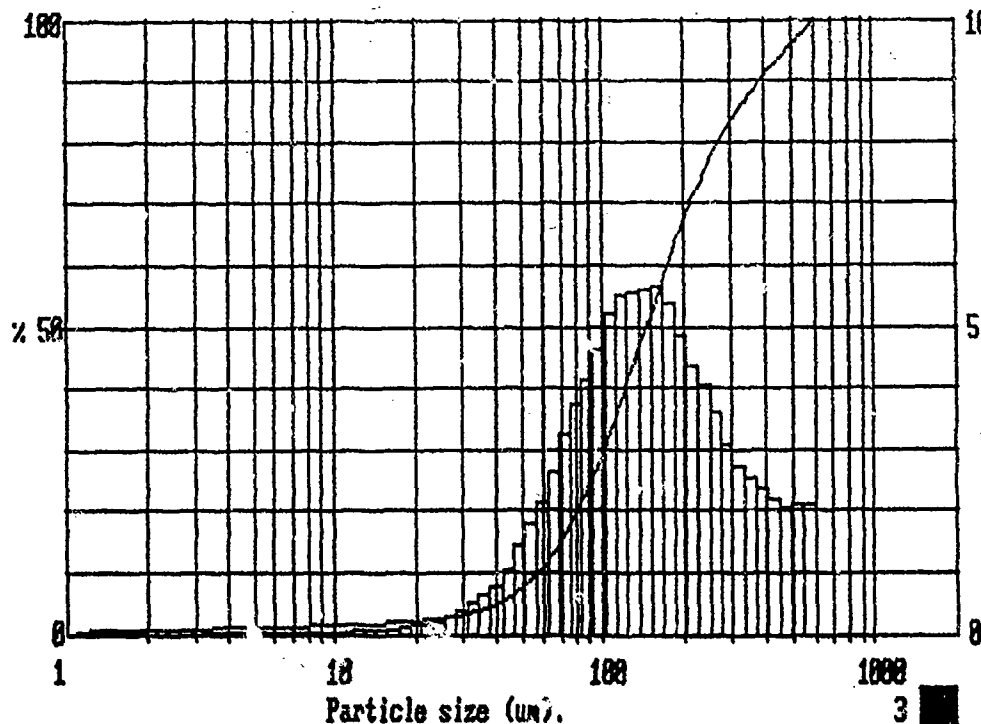
MALVERN MasterSizer/E SB.02 Easy Mode 20 Aug 1993 9:40 am

High Size	Under %	High Size	Under %	High Size	Under %	High Size	Under %	High Size	Under %	High Size	Under %	Span 2.24
600	100	203	68.5	68.5	14.7	23.1	2.6	7.82	1.5	2.64	0.9	D(4,31)
544	97.9	184	63.8	62.1	12.0	21.0	2.4	7.08	1.5	2.39	0.8	181.68µm
493	95.8	166	58.2	56.2	9.8	19.0	2.3	6.42	1.4	2.17	0.8	D(3,21)
442	93.7	151	52.5	50.9	8.0	17.2	2.1	5.83	1.4	1.97	0.7	57.73µm
404	91.5	137	46.9	46.2	6.6	15.6	2.0	5.27	1.3	1.78	0.6	D(2,11)
366	89.1	124	41.3	41.8	5.5	14.1	1.9	4.77	1.3	1.61	0.5	D(1,0.91)
332	86.5	112	35.8	37.9	4.7	12.8	1.8	4.33	1.2	1.46	0.4	380.59µm
301	83.7	102	30.9	34.3	4.0	11.6	1.8	3.92	1.2	1.32	0.3	D(0.5,1)
273	80.6	92.1	25.9	31.1	3.5	10.5	1.7	3.55	1.1	1.20	0.2	144.36µm
247	77.0	83.4	21.7	28.2	3.1	9.52	1.6	3.22	1.1			
224	72.9	75.6	18.0	25.5	2.8	8.63	1.6	2.92	1.0			

Source = Data:p81-91rp Beam length = 15.0 mm Model indep
 Record No. = 1 Residual = 1.366 %
 Focal length = 300 mm Obscuration = 0.1797 Volume Conc. = 0.0249%
 Presentation = std Volume distribution Sp.S.A 0.1038 m²/cc.

7033 std IM10133V
 Coarse Ammonium Sulphate
 LR P81/91

MALVERN MasterSizer/E SB.02 Master Mode 20 Aug 1993 9:48 am



7033 std IM10133V
 Coarse Ammonium Sulphate
 LR P81/91

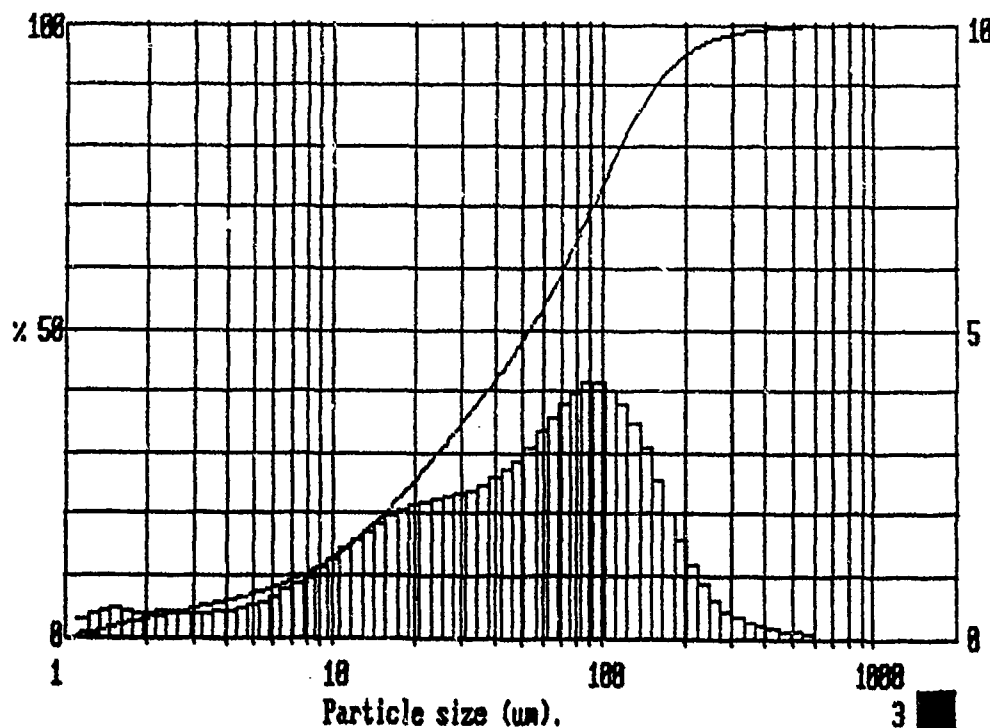
Figure 2: Typical ammonium sulphate (coarse) particle size data from Malvern Mastersizer/E analyser.

MALVERN MasterSizer/E SB.0B Easy Mode 24 Oct 1919 4:17 pm

High Size	Under %	High Size	Under %	High Size	Under %	High Size	Under %	High Size	Under %	High Size	Under %	Span
600	100	203	95.5	68.5	58.8	23.1	28.8	7.82	10.3	2.64	4.3	D[4,3]
544	99.9	184	93.9	62.1	55.2	21.0	26.6	7.08	9.4	2.39	3.8	71.43µm
493	99.8	166	91.8	56.3	51.8	19.0	24.4	6.42	8.6	2.17	3.4	
446	99.6	151	89.8	50.9	48.7	17.2	22.3	5.82	7.9	1.97	3.0	D[3,2]
404	99.4	137	86.2	46.2	45.3	15.6	20.3	5.27	7.4	1.78	2.6	14.47µm
366	99.2	124	82.7	41.8	43.1	14.1	18.5	4.77	6.8	1.61	2.2	
332	99.0	112	78.9	37.9	40.5	12.8	16.7	4.33	6.4	1.46	1.7	D[v,0.9]
301	98.6	102	74.9	34.3	38.1	11.6	15.1	3.92	5.9	1.32	1.2	154.65µm
273	98.2	92.1	70.7	31.1	35.7	10.5	13.7	3.55	5.5	1.20	0.8	
247	97.5	83.4	66.5	28.2	33.3	9.52	12.4	3.22	5.1			D[v,0.1]
224	96.7	75.6	62.6	25.5	31.0	8.63	11.3	2.92	4.7			7.59µm
Source = Data:ASul			Beam length = 15.0 mm			Model indp						
Record No. = 3			Residual = 0.424 %			Volume Conc. = 0.0073%						D[v,0.5]
Focal length = 300 mm			Obscuration = 0.2093			Sp.S.A 0.4147 m ² /cc.						53.11µm
Presentation = std			Volume distribution									

7033 std IM10133Y
Ammonium Sulphate Fine
Run Number 3

MALVERN MasterSizer/E SB.0B Master Mode 24 Oct 1919 4:17 pm



7033 std IM10133Y
Ammonium Sulphate Fine
Run Number 3

Figure 3: Typical ammonium sulphate (fine) particle size data from Malvern Mastersizer/E analyser.

The agreement between the measured values and the values provided with the materials is reasonable. The results show that there may have been some agglomeration of the ammonium sulphate over the period of testing. The agreement between the two instruments appears to be acceptable, except for the fine ammonium sulphate; while no explanation can be given for the apparently high values of 69 and 79 μm , they may have been due to sampling problems. A breakdown of the Malvern LBD prevented the making of repeat measurements on the fine ammonium sulphate.

The reason that the frequency curve for the coarse ammonium sulphate measured on the Mastersizer/E did not go to zero at large sizes (see Fig. 2), is that the instrument has an upper particle size limit of 600 μm , and all particles above this size are lumped into the 600 μm band.

A sieve analysis was made of the coarse ammonium sulphate. The median diameter was 220 μm , which is in good agreement with the light scattering values. The amounts retained on the sieves were as follows:-

Sieve Sizes in μm		Amount (%)
Retained on	425	11.44
Through	425 on 355	10.26
Through	355 on 300	11.41
Through	300 on 212	17.50
Through	212 on 150	16.74
Through	150	33.10

3. Rheology

3.1 Mixing Procedure

The material studied was mixed from the ingredients provided as part of the KTA. It was intended to reproduce the conditions of the original master batch as closely as possible, and the mix procedure is summarised below.

Mixer:	1 gallon Baker Perkins vertical propellant mixer	
Blade speed:	40 rpm	
Composition:	Material	Level (% w/w)
	HTPB	13.0
	Aluminium	16.4
	Ammonium Sulphate (coarse)	49.5
	Ammonium sulphate (fine)	21.1

Mix procedure:

Step	Material added	Temp (°C)	Mix time	
			No vacuum	Vacuum
1	HTPB	60	0	45
2	2/3 AS (coarse)	55	2	13
3	2/3 AS (fine)	55	2	13
4	1/3 AS (coarse)	50	2	13
5	1/3 AS (fine)	50	2	13
6	Aluminium	50	-	45

The material was stored in a sealed paint tin until required. Testing was carried out over a period of a week, and settling of the contents over this time was expected to be minimal. Before testing, samples were maintained at 60°C for at least one hour either in an oven or in the test instrument.

3.2 Rotary Viscometry

3.2.1 Equipment

Viscosity was measured with a Haake RV3 Rotovisco 3 viscometer using a modified Couette geometry. The material being tested was placed in the annular space between a stationary cup and a rotor driven through a torque measuring head by a motor. The drive speed of the motor was reduced by a gearbox with a ratio of 100:1. Two measuring heads were used:

Maximum Torque

DMK 50/500	0.0049/0.049 Nm	(50/500 gcm)
MK 5000	0.49 Nm	(5000 gcm)

A torque measuring head consists of a torsion spring mounted between the drive shaft and the rotor spindle, and a rotary potentiometer which measures the displacement of the spring in response to applied torque. The stiffness of the spring was relatively low, so that at low rotation rates and high sample viscosities the displacement took a number of hours to reach equilibrium. This meant that it was often only possible to do one run per day.

Three different cup and rotor combinations were used:

	Rotor radius (mm)	Cup radius (mm)	Gap (mm)
MVII	18.4	21.0	2.6
MVIIP	18.4	21.0	2.6
MVIII	15.2	21.0	5.8

The MVIIP cup and rotor had the same dimensions as the MVII cup and rotor, but the surfaces were grooved to eliminate wall slip.

Temperature was controlled with a water jacket and a thermocirculator, and the temperature of the circulating water was maintained at $60.0^\circ \pm 0.1^\circ\text{C}$.

Torque measurements were recorded with a computer controlled data logger, and the results were analysed and plotted using spreadsheet software. Torque was calibrated by mounting the measuring head horizontally and attaching various weights to a thin wire wrapped around the rotor. Shear stress and shear rate values were obtained from torque and rotation speed using factors provided in the instrument manual.

Measurements were made by starting at the lowest rate and waiting until an equilibrium torque level was reached, which was recorded. The rotation rate was then stepped up to the next rate, and the process repeated until the limit of the measuring head was reached, or gross slip was observed.

3.2.2 Results and Discussion

Measurements were made using all three cup and rotor sets with the DMK 50/500 measuring head in the 0.049 Nm (500 gcm) range, and the MVIIP cup and rotor were also used with the MK 5000 measuring head. As noted in the previous section, it was often only possible to make measurements with one cup and rotor set in a day because of the long time taken by the torque to reach equilibrium values. The length of time taken to make the measurements meant that there were varying delays between time of mixing and testing. The effect of the delays will be discussed later.

An example of the flow start-up behaviour at very low shear rates is given in Figure 4. The change of torque with time after start-up in the MVIIP cup and rotor with the DMK 50/500 head at an apparent shear rate of 0.0036 s^{-1} is shown (the unit of shear rate, reciprocal seconds, will be designated " s^{-1} "). The measurements were made one day after mixing. The torque reached the minimum value, taken to be the equilibrium value, after about 500 readings. The time per point was 80 s, so the total time taken to reach equilibrium was approximately 40 000 s, or 11 h. The total strain to equilibrium, obtained from the product of the nominal shear rate and time, was about 144.

A second example of start-up behaviour in the MVIIP cup and rotor is given in Figure 5. The measurements were made four days after mixing. The lowest curve shows the time evolution of torque at a shear rate of 0.0072 s^{-1} . The time per point was 16 s, so the time to equilibrium was about 8000 s, and the total strain was about 58. These values are lower than those for the shear rate of 0.0036 s^{-1} , and the difference may be due to the high compliance of the Haake instrument which would have smeared the response over time to different extents for different shear rates.

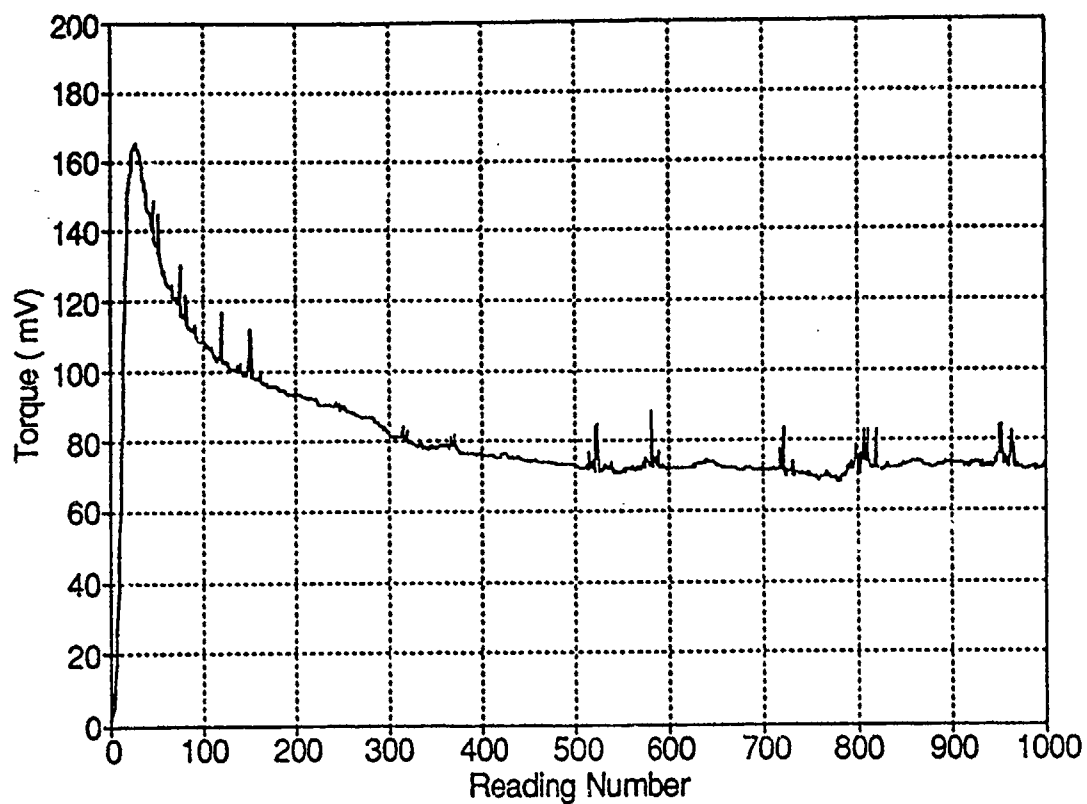


Figure 4: Transient torque curves from start-up of flow, Haake viscometer with MVIIP cup and rotor, shear rate 0.0036 s^{-1} . Time per point 80 seconds.

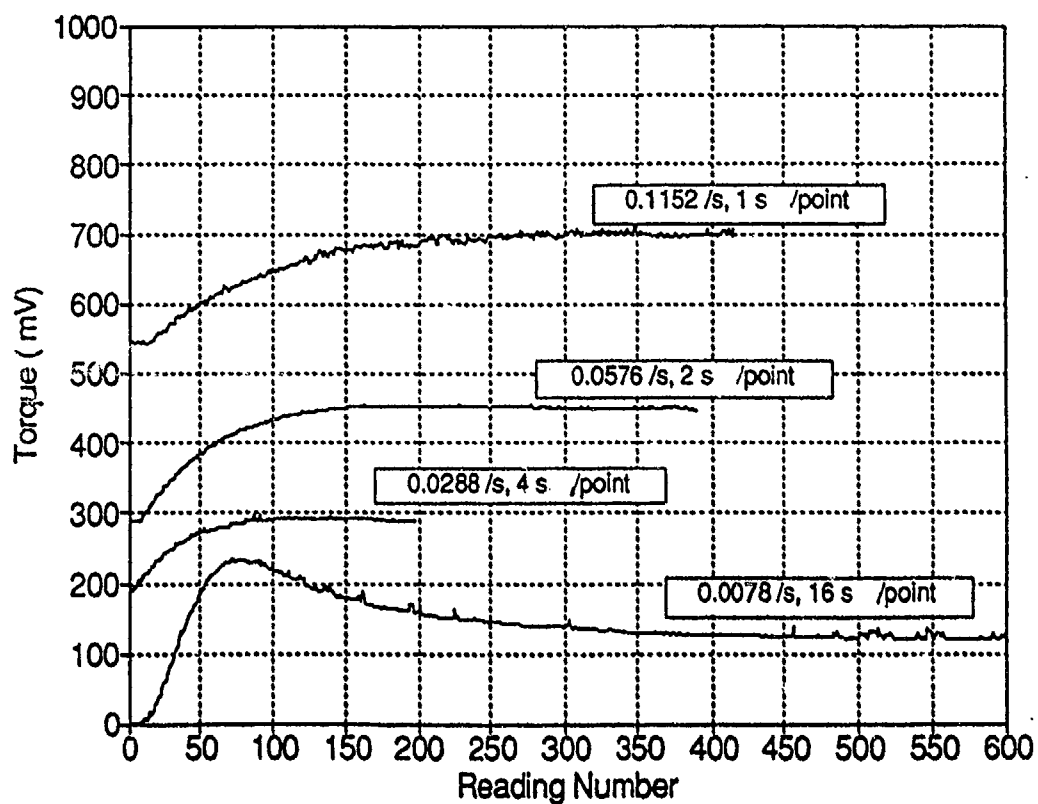


Figure 5: Transient torque curves from start-up of flow, and from step increases in shear rate, Haake viscometer with MVIIP cup and rotor.

Torque curves for stepping up the shear rate to values of 0.0288 s^{-1} , 0.0576 s^{-1} , and 0.115 s^{-1} are also given in Figure 5. Unfortunately the data for the shear rate 0.0144 s^{-1} were lost. It can be seen that after the initial curve the torque increased to the equilibrium value monotonically. Since the times per point were decreased in proportion to the increase in shear rate, the similar shape of the curves indicates that equilibrium torque was reached after a constant shear strain.

The start-up behaviour in the smooth walled cups and rotors was different from the profiled ones. The stress rose monotonically to the equilibrium values without an overshoot, except possibly at the highest rate.

Because the time taken for a run was often the major part of a day, the series of measurements had to be made over a period of many days. It was noticed that when a repeat run was made after several days the viscosity appeared to be higher than that of the original run. A further complication was that testing was not started until four days after the initial mixing of the material. To enable further results to be obtained from material which had suffered a minimum delay after mixing, all the material that had been tested was combined with the untested material, and the lot was remixed for 30 minutes under the same mixing conditions that were used for the final stage of the original mix. This material was then treated as fresh material for the purpose of calculating delays in measurement.

The results obtained from the MVIIP cup and rotor and the MK 5000 head at three different ageing periods after mixing are plotted in Figure 6. The curve for 0 days was obtained from remixed material that was tested within a few minutes from the end of mix. The curves obtained after five and eight days were obtained from fresh material. It can be seen that the viscosity does appear to increase significantly with increasing delay from mixing. A similar trend is seen with the MVIIP and DMK 50/500 combination in Figure 7 (note the difference in shear rate scale).

The results obtained with the smooth walled MVII cup and rotor with the DMK 50/500 head are shown in Figure 8. In this case the curves for one day and five days delay are very close, but the one day curve is above the five day curve, contrary to the previous observations, but this difference is probably not significant.

Only one flow curve was obtained for the MVIII cup and rotor, and it is given in Figure 9.

A composite plot of the flow curves from various cup and rotor sets and measuring heads is given in Figure 10. Where multiple runs were made with the same setup, the curve plotted was the one for the minimum delay after mixing. The two curves for the MVIIP cup and rotor with the DMK 50/500 and MK 5000 heads would be expected to superimpose, but in fact they are displaced by a considerable amount. Part of the reason for the poor agreement may be that the MK 5000 curve was obtained immediately after mixing, but there was a delay of one day in obtaining the DMK 50/500 curve.

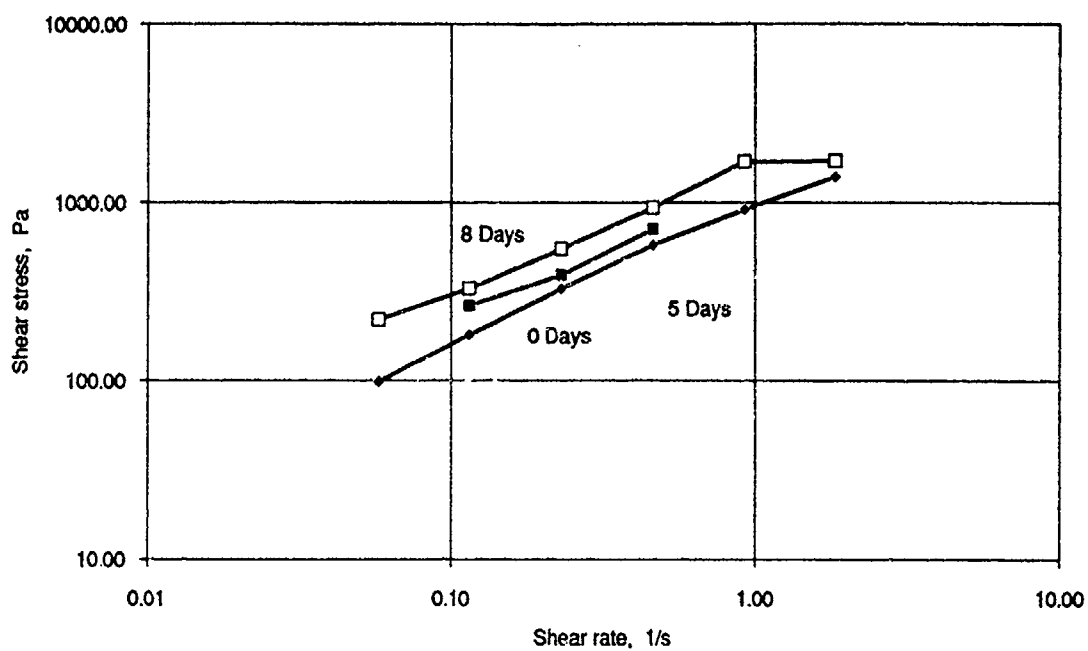


Figure 6: Flow curves of shear stress vs shear rate. Haake viscometer with MVIIP cup and rotor, DM 5000 measuring head. Runs made at nominated delays from time of mixing.

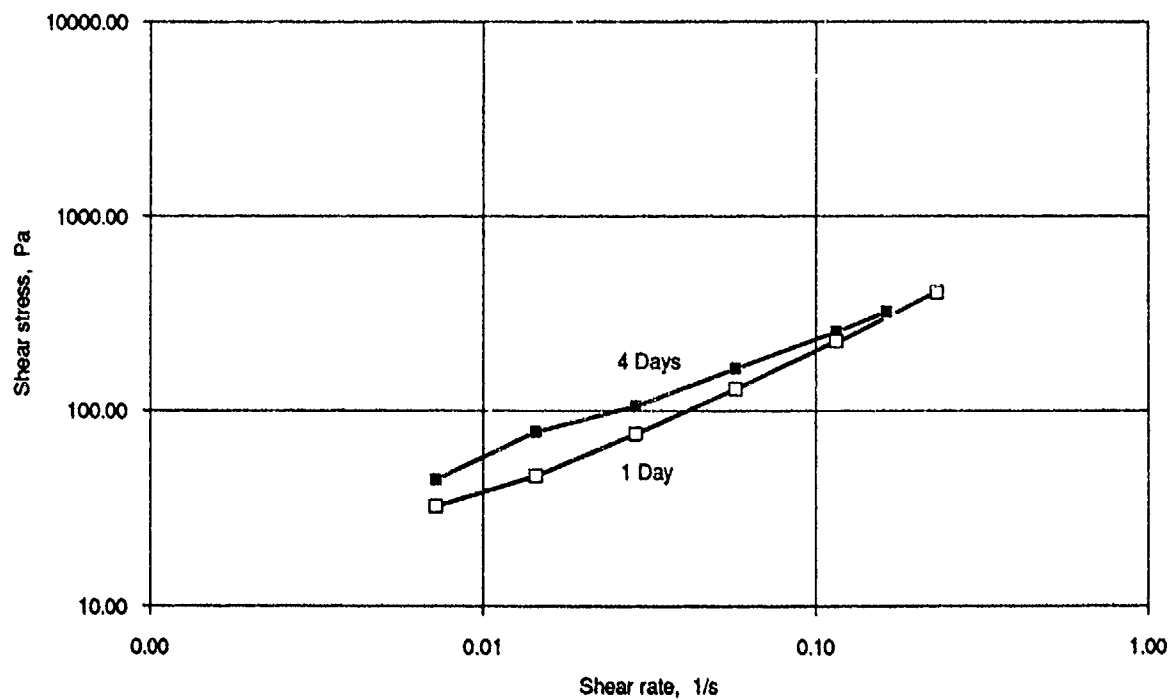


Figure 7: Flow curves of shear stress vs shear rate. Haake viscometer with MVIIP cup and rotor, DMK 50/500 measuring head. Runs made at nominated delays from time of mixing.

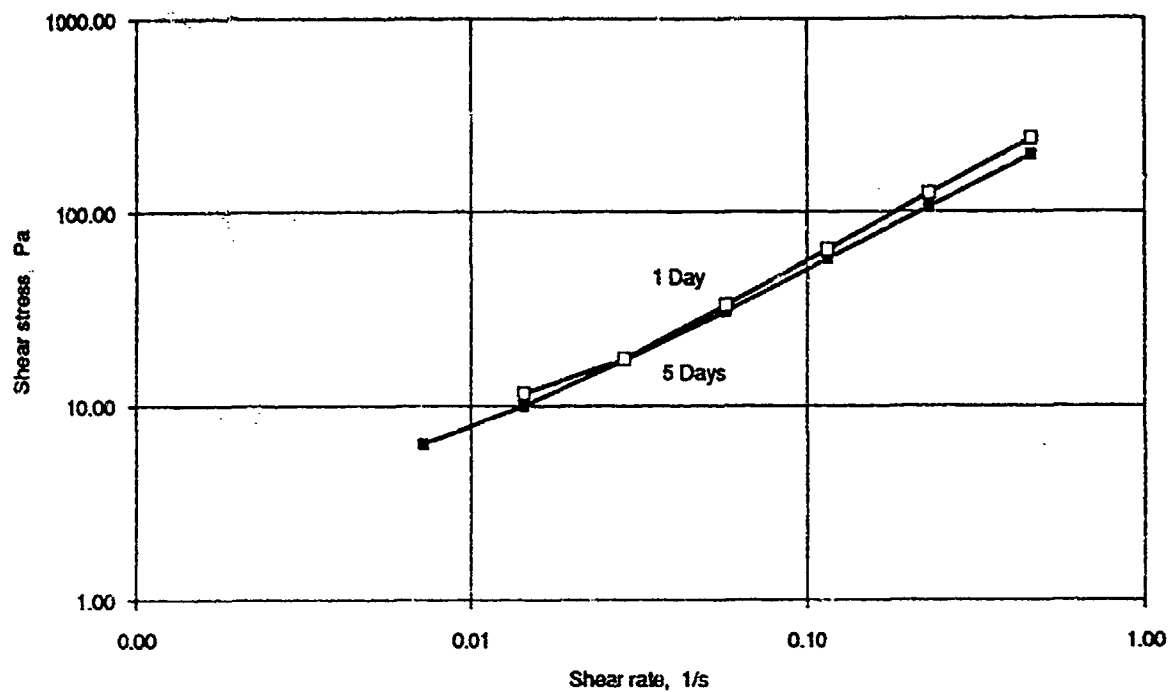


Figure 8: Flow curves of shear stress vs shear rate. Haake viscometer with MVII cup and rotor, DMK 50/500 measuring head. Runs made at nominated delays from time of mixing.

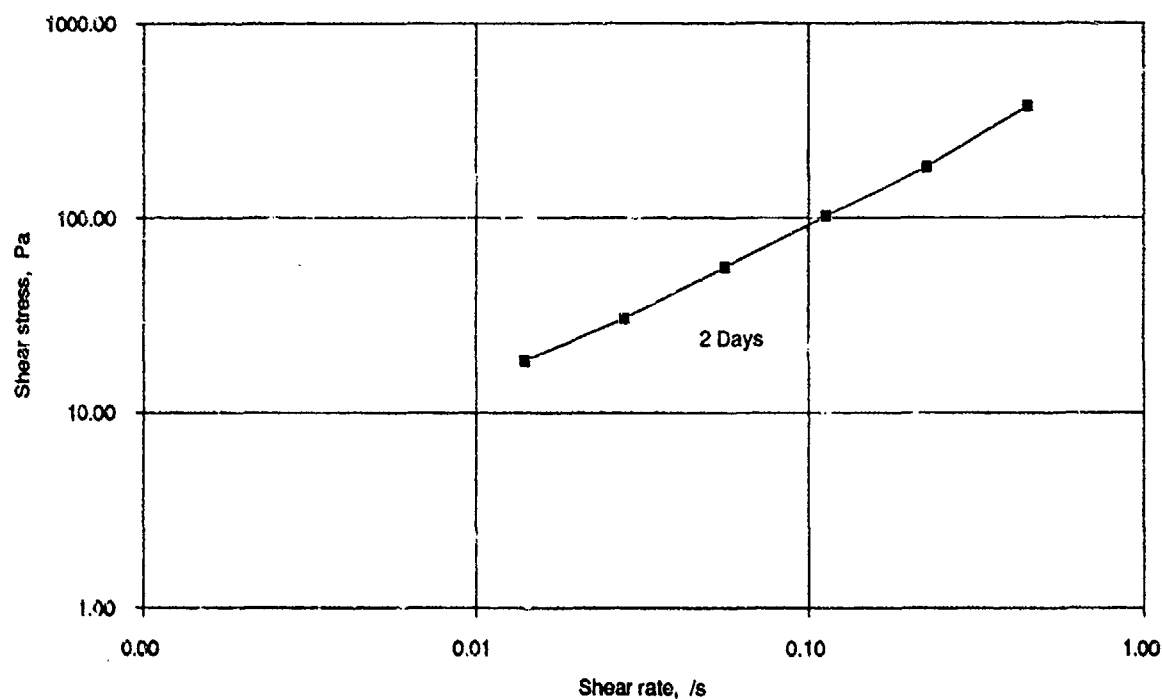


Figure 9: Flow curves of shear stress vs shear rate, Haake viscometer with MVIII cup and rotor, DMK 50/500 measuring head.

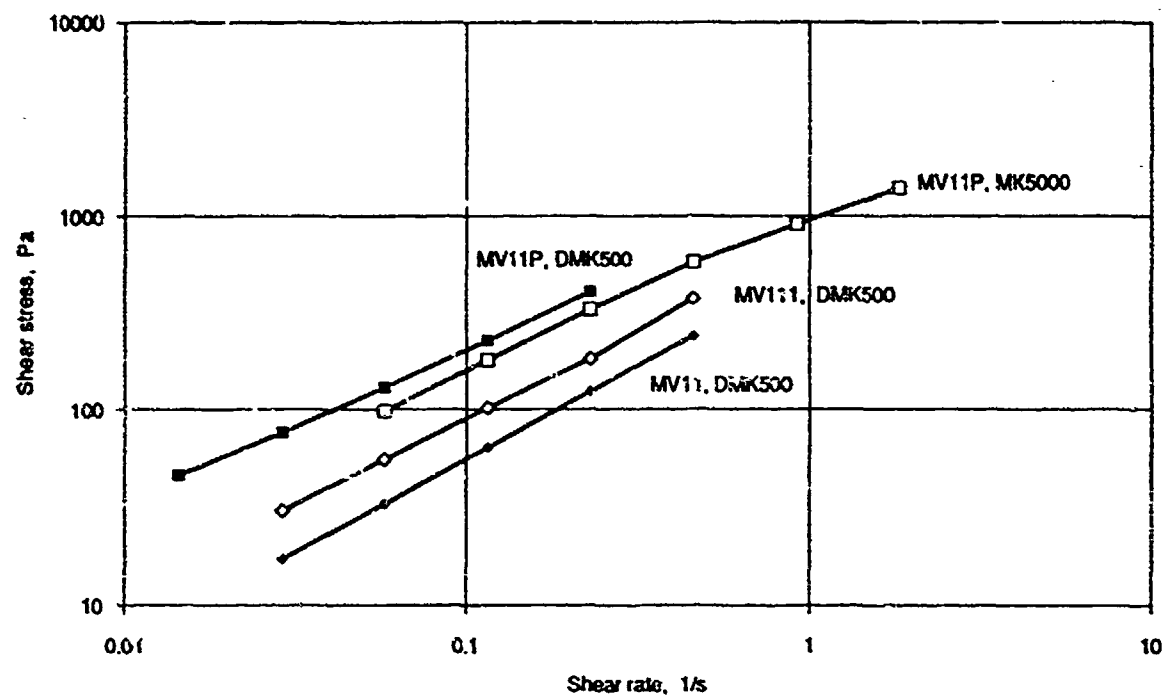


Figure 10: Flow curves of shear stress vs shear rate, Haake viscometer with MVIIP, MVII, MVIII cups and rotors, DMK 50/500 and DM 5000 measuring heads.

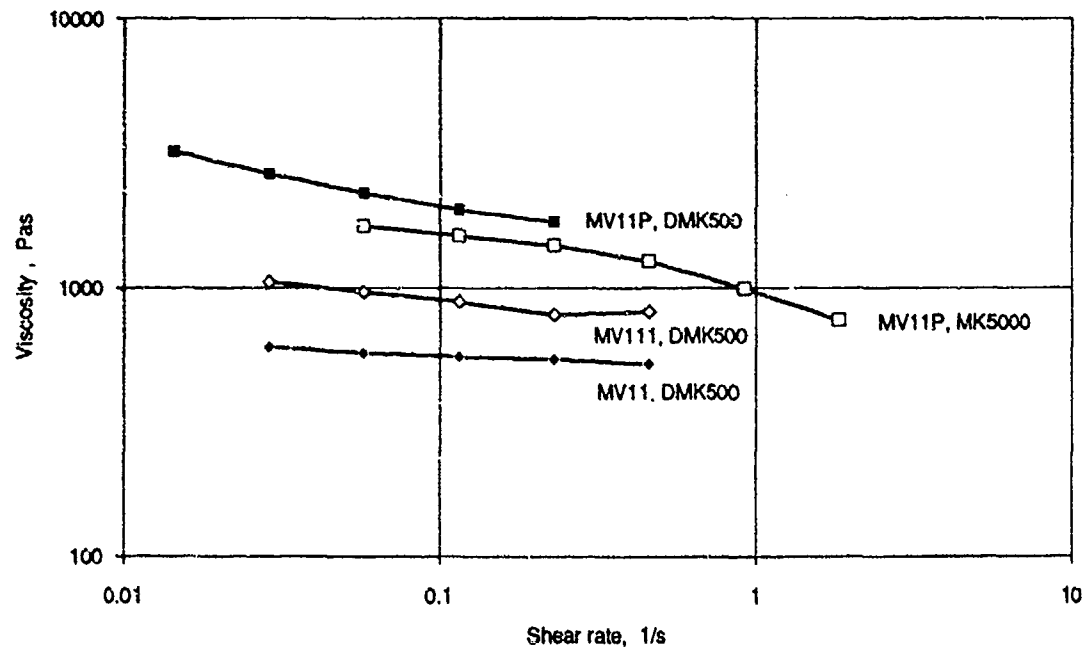


Figure 11: Viscosity vs shear rate, Haake viscometer with MVIIP, MVII, MVIII cups and rotors, DMK 50/500 and DM 5000 measuring heads.

Curves of the viscosity vs shear rate are given in Figure 11. The profiled cup and rotor set gave the highest apparent viscosity, followed by the wide gapped MVIII, and then the MVII. The stresses and viscosities were calculated on the assumption that the material was Newtonian and that there was no slip at the walls. Both these assumptions are incorrect. The MVIIP curves have a negative slope of about 0.2, which indicates a mild departure from a Newtonian viscosity. In addition, the fact that the apparent viscosity decreased with decreasing gap in the smooth walled cups and rotors indicates that some form of wall slip was occurring, and this behaviour will be discussed in detail in Section 4.

3.3 Extrusion Rheometry

3.3.1 Equipment

The extrusion rheometer consisted of a water jacketed steel barrel with an internal diameter of 32 mm and a length of 180 mm, and a ram driven at a range of constant rates by a model TTCM Instron machine. A water jacketed slit die was mounted on the bottom of the barrel. The slit channel was 0.98 mm thick, 10 mm wide, and 80 mm long. Shims could be used to increase the slit thickness to 1.96 mm. The entrance to the slit was tapered. A Terwin pressure transducer was flush mounted in the slit wall 46.5 mm from the die exit. Measurements were made at a die temperature of $60.0^\circ \pm 0.1^\circ\text{C}$.

3.3.2 Results and Discussion

The extrusion measurements were made after approximately the same periods of ageing as the rotary viscosity measurements. The flow curves obtained with the 1 mm slit after delays of 0, 4, and 6 days are given in Figure 12. The 0 day run was made immediately after remixing. The curves for the two shortest delays agree very well, but the curve for the longest delay is significantly higher. The differences in the curves may be partly due to a change in viscosity on ageing after mixing.

Flow curves for the 2 mm thick die obtained after delays of four and five days are given in Figure 13. It can be seen that the agreement is very good.

A composite plot of the curves from the two slit thicknesses is given in Figure 14. The curves are of the shortest delay data. The slopes of the curves are very close to 1, indicating that the apparent viscosity is close to Newtonian. The curve from the 1 mm slit is significantly below the 2 mm curve, indicating that an apparent wall slip occurred, as discussed in the next section.

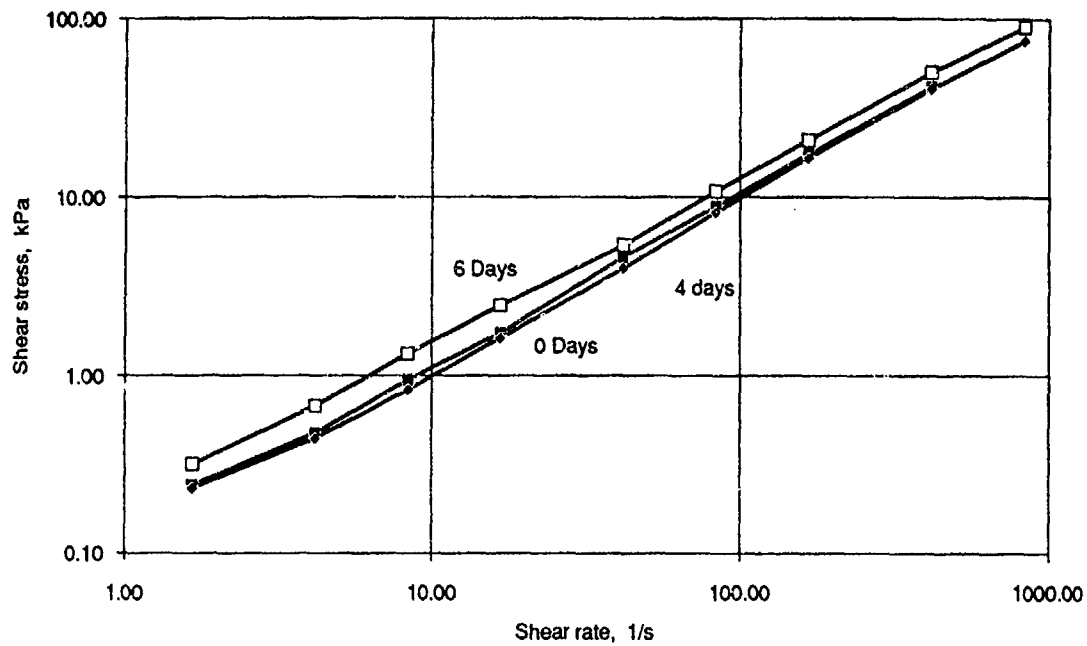


Figure 12: Flow curves of extrusion shear stress vs shear rate, 1 mm slit thickness. Runs made at nominated delays from time of mixing.

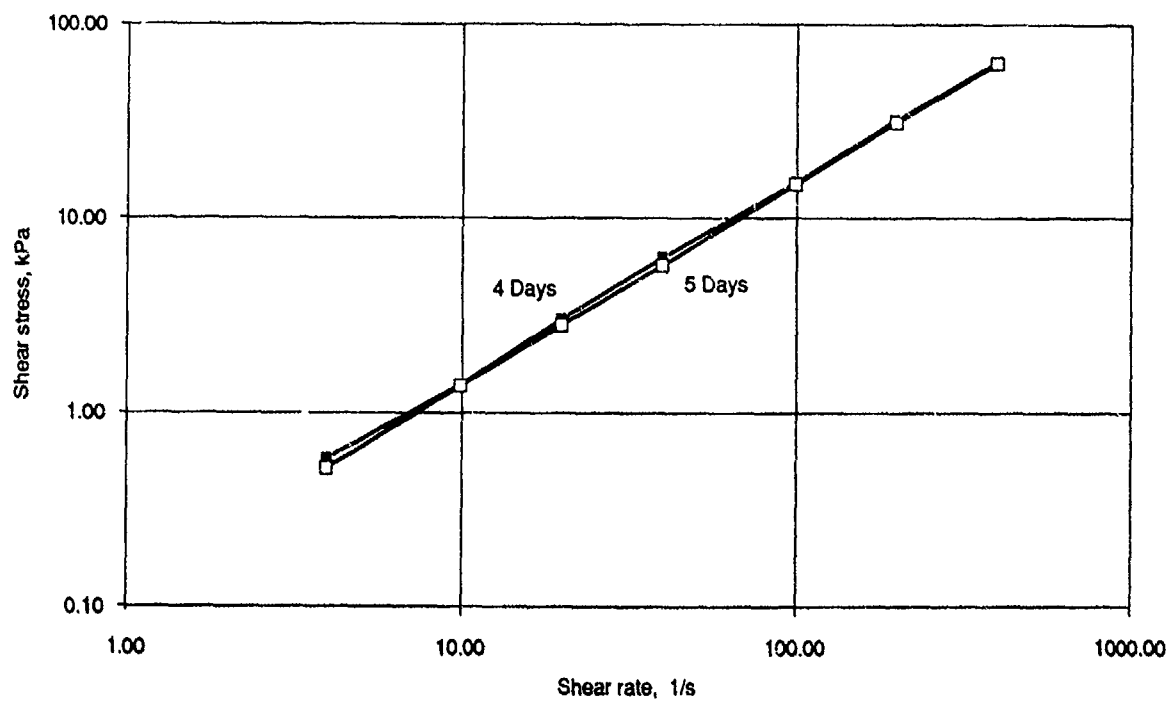


Figure 13: Flow curves of extrusion shear stress vs shear rate, 2 mm slit thickness. Runs made at nominated delays from time of mixing.

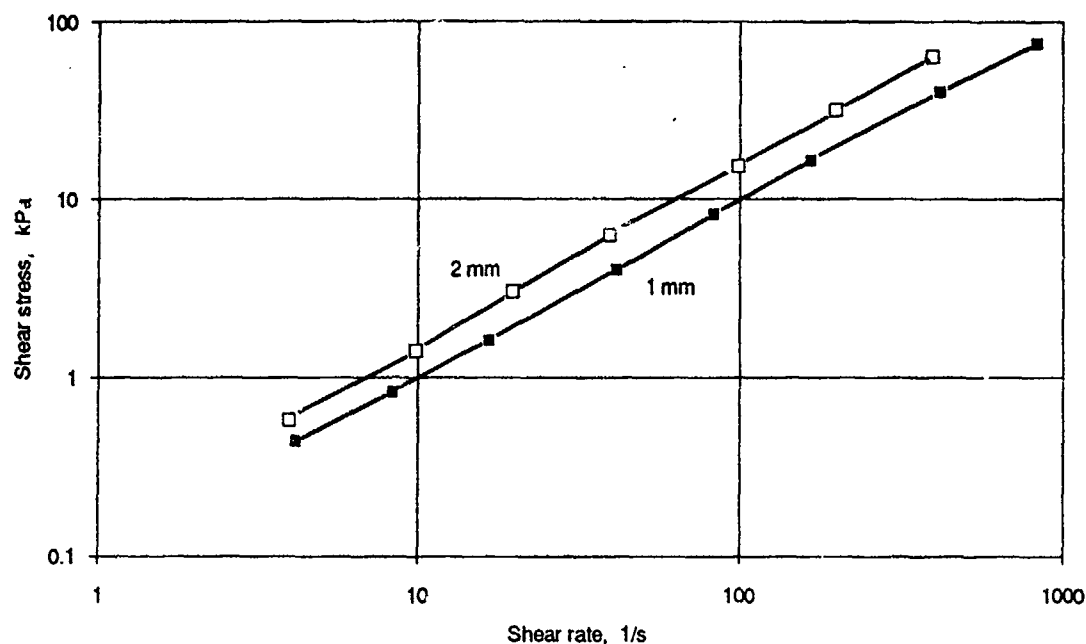


Figure 14: Flow curves of extrusion shear stress vs shear rate, 1 and 2 mm slit thicknesses.

4. General Discussion

A composite plot of the rotary and extrusion shear stress vs shear rate data is given in Figure 15, and the corresponding plot of viscosities is given in Figure 16. It can be seen that the curves for the extrusion data are below the curves for the rotary data. The slopes of the extrusion viscosity curves are essentially zero, whereas the slopes of the rotary viscosity curves have varying negative values.

It is believed that the explanation of the complex flow behaviour is an apparent slip at the walls caused by the formation of a binder rich layer which effectively lubricated the flow of the bulk of the material. It has long been known that filler particles tend to migrate away from the high shear region near the walls, leaving a thin layer of binder against the wall, and this behaviour has been reported for propellant analogues [1, 2]. A recently reported imaging NMR study on model materials has confirmed this behaviour [3]. As a result, the flow deformation is partitioned between the low viscosity binder layer and the high viscosity bulk material.

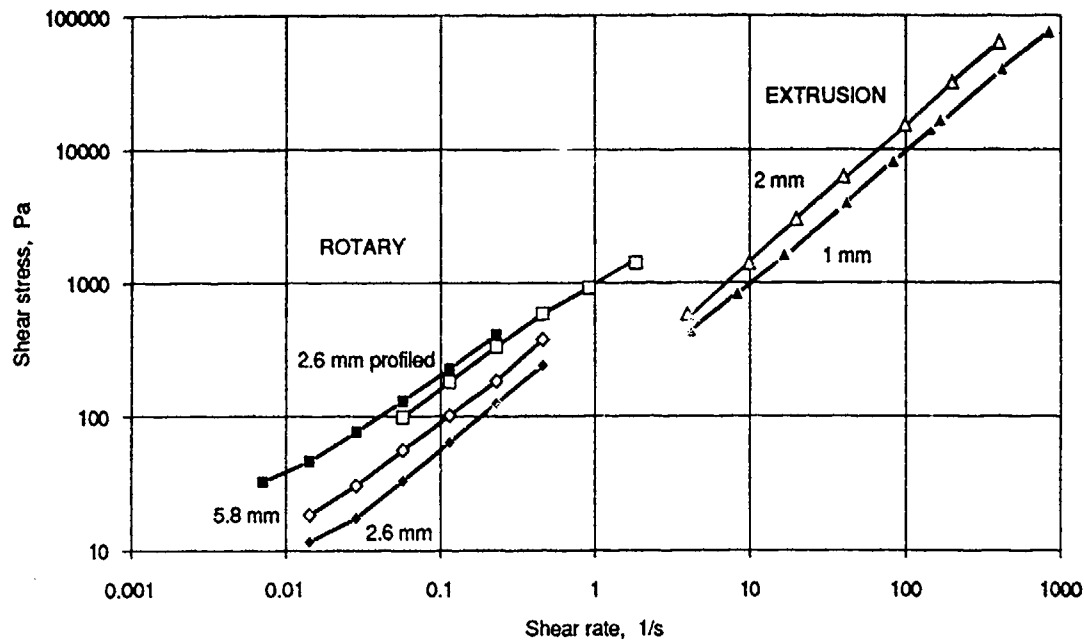


Figure 15: Flow curves of shear stress vs shear rate, Haake viscometer with MVIIP (2.6 mm), MVIII (5.8 mm) cups and rotors, DMK 50/500 and DM 5000 measuring heads, and extrusion rheometer with 1 and 2 mm slit thicknesses. Haake gap thicknesses are given in brackets.

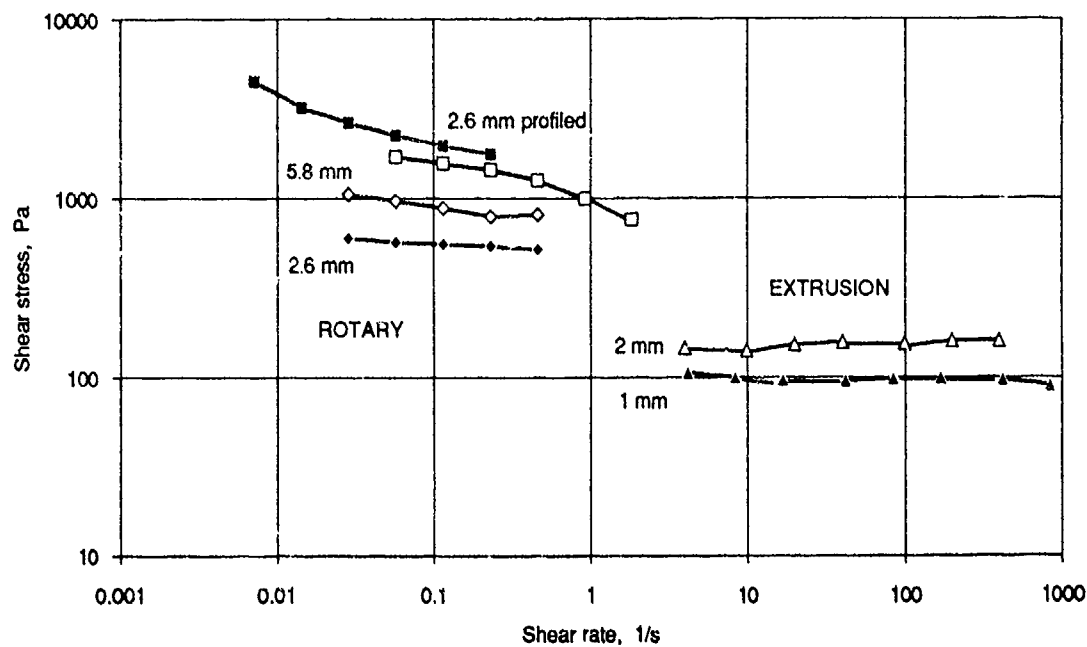


Figure 16: Viscosity vs shear rate, Haake viscometer with MVIIP (2.6 mm), MVII (2.6 mm), MVIII (5.8 mm) cups and rotors, DMK 50/500 and DM 5000 measuring heads, and extrusion rheometer with 1 and 2 mm slit thicknesses. Haake gap thicknesses are given in brackets.

For very thick flow channels the effect of the binder layers is relatively small, and the apparent viscosity is close to the viscosity of the bulk of the material. However, for thin flow channels the thickness of the low viscosity wall layers is relatively large, and hence the apparent viscosity is greatly reduced. The curves in Figures 15 and 16 show that the narrower gap in both rotary and extrusion rheometry gave lower calculated shear stresses and viscosities.

The slopes of the viscosity vs shear rate curves from the different cups and rotors have different values; see Figure 11. The profiled cup and rotor has the highest negative slope of about - 0.2, which indicates that the material is shear thinning to a small extent. At high shear rates the slope of the curve increases, which may indicate the onset of non-uniform flow. The slope of the curve from the thin gapped smooth MVII cup and rotor has a small slope of about - 0.05, indicating that the flow is dominated by the layer of binder, which has a Newtonian viscosity. The curve from the wide gapped MVIII has a slope of about - 0.1, which is intermediate between the other two curves. This indicates that the flow behaviour is being determined to an approximately equal extent by the binder layer and the bulk of the material.

The gap thicknesses for the rotary instrument are 2.6 and 5.8 mm, and for the slits the thicknesses are 1 and 2 mm. It might be expected at first sight that the curve from the 2.6 mm gap in the rotary rheometer and the curve from the 2 mm slit would be fairly close. However, this is not the case, see Figure 16. The reason is that in the rotary rheometer the highest shear region is adjacent to the rotor, and this is where the single binder layer forms. This effect has been observed in an NMR study [3]. In the extrusion case there are two binder layers formed, one on each side of the slit, so the effect of slip is approximately twice as great as in the rotary case, and the calculated shear stresses are correspondingly lower.

There are several procedures for correcting the effect of apparent slip at the wall using data obtained with different gap or slit thicknesses. The first method for capillary and Couette geometries was developed by Mooney [4], but simpler methods for the Couette geometry have been reported recently [5, 6]. Corrections could have been applied to the data here, but it was felt that the uncertainties in the data caused by the effect of different delays in taking measurements would have reduced the accuracy of the corrections and possibly given misleading results.

It is possible that profiled slit dies, with fine grooves in the wall perpendicular to the flow direction, may overcome some of the problems with apparent wall slip. However, it is likely that at higher shear rates a fracture layer would develop above the tops of the grooves, and the effect of the profiling would be lost.

The flow of the binder layer should be independent of any structural change in the filler taking place in the bulk of the material. The flow curves from the smooth sensors, which are strongly affected by the binder layer, would not be expected to show a large effect of ageing of the bulk material. Hence, the two flow curves obtained on different days with the smooth MVII cup and rotor should be very similar, and the difference between the curves in Figure 8 may be due to random experimental error.

Viscosity measurements on composite materials are essentially transient, because the migration of the filler takes a finite time. The curves in Figures 4 and 5 show that large strains are required for the wall layer to stabilise in profiled cups and rotors in Couette flow. The situation in smooth walled cups and rotors

may be somewhat different. In this case a layer of binder should form at the wall relatively quickly and lubricate the flow of the bulk material, and the shear stress should appear to reach equilibrium in a short time. However, the bulk of the material is still undergoing deformation, albeit at a very low rate, and so particle migration should continue and the surface layer should grow in thickness. This suggests that at long times the flow should be similar to the flow in profiled cups and rotors. There was some suggestion of an overshoot in torque vs time curves obtained at high rates, but this behaviour would be difficult to study because of the long times involved.

In order to accurately follow the development of stress with time, the measuring instrument should have a low compliance, i.e. the deformation of the instrument under test conditions should be small. This requirement reduces the suitability of the Haake viscometer because its compliance is inherently high. Other instruments such as the Rheometrics Mechanical Spectrometer may be more suitable for transient measurements.

This study raises a number of issues which will have to be addressed in future work. The possibility of change occurring in rheological properties over a period of days after mixing should be checked. If the effect is found to be real it poses difficulties in the design of collaborative experiments. One way of overcoming this problem, and also allowing the transport of material between laboratories in round-robin studies, would be to use a stable binder which solidifies at room temperature, but is a liquid at processing temperature. A master batch could be made, and then stored in a solid form at room temperature, where the filler would be effectively immobilised until the material was heated for use.

It would appear that the greatest obstacle to achieving reproducible rheological measurements is filler particle migration during testing. Any future collaborative studies in this area should give high priority to investigation of this phenomenon.

5. Conclusions

This study has highlighted some of the complexities of the flow of composite materials, and demonstrated the need for improvements to rheological test procedures for composite propellants in Australia. It has vindicated the proposition that the rheology of energetic materials is an area worthy of a large scale cooperative study. However, because of difficulties with the transport of the master batch, and other experimental problems, it has not been possible to produce quantitative data for comparison with other laboratories.

The flow behaviour of composite propellants has been found to be inherently time dependent because the filler particles migrate in non-uniform stress fields to regions of low shear stress. The level of strain in a rotary viscometer needed to be applied to produce an equilibrium filler distribution, and hence a constant viscosity, is of the order of tens of strain units.

The filler migration causes a layer of binder to develop at the walls confining flow, and this layer lubricates the flow of the bulk of the material causing an apparent slip. The effect of the slip is to reduce the apparent viscosity of the material.

At low shear rates in the Couette geometry the effect of apparent wall slip can be overcome by the use of profiled cups and rotors. The torques obtained with

profiled cups and rotors are much greater than those obtained from smooth units at the same rotation rates.

The flow in slit extrusion dies appears to be Newtonian, because the overall flow is dominated by apparent slip in layers of binder next to the slit walls. The apparent viscosity obtained from extrusion is lower than that obtained from rotary viscometry.

The particle size determinations were in reasonable agreement with the values provided with the materials.

6. Acknowledgements

The author would like to thank Mr P.M. Whitehead for assistance with the rheology and particle size measurements and Mr P. Rawson for mixing the samples.

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Some problems in the rheological characterisation of composite rocket propellants

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ABSTRACT

Apparent viscosities of a composite propellant analogue were measured with both rotary and extrusion instruments. A Haake Viscometer in the Couette configuration was used with 2 gap widths and also with a profiled cup and rotor. An extrusion rheometer was fitted with a slit die and measurements were made at 2 slit thicknesses. The flow was found to be time dependent, and there was apparent slip at the wall. It is suggested that the cause of this behaviour is filler particle migration in the non-uniform stress fields. The filler migration is assumed to cause a layer of binder to develop at the walls confining the flow, and this layer would lubricate the flow of the bulk of the material causing an apparent slip. The effect of the slip is to reduce the apparent viscosity of the material, which also appears to be affected by ageing of the samples under ambient conditions for several days. Particle sizes of the solid ingredients were also measured.

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SUPPLEMENTARY

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Corrigendum

Please note the following correction to this report.

Page 21: Figure 16 -

**The axis in Figure 16 should read "Viscosity, Pas" instead of
"Shear stress, Pa"**

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